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TECHNICAL REPORT

FD-16

DEVELOPMENT OF IRRADIATION STERILIZED
SHELF-STABLE FISH AND SEAFOOD PRODUCTS

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by

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OREGON STATE UNIVERSITY
Department of Food Science and Technology
Corvallis, Oregon

Contract No. DA 19-129-QM-1356

August 1965

U. S. Army Materiel Command
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts



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FOREWORD

The availability of shelf-stable, highly acceptable fish and seafood products for use in military feeding systems is considered a necessity. The currently available thermally processed items do not fully meet requirements because of their limited utility, stability and acceptability. Radiation processing, or "cold" sterilization as it is frequently called, has the potentiality of yielding products that have good military utility, good storage stability, and good acceptability. Therefore, research to develop process criteria that can be used to produce irradiation sterilized fish and seafood products is underway.

The work covered in this report was performed by Oregon State University under Contract DA19-129-QM-1316 during the period from January 1959 to June 1963. It represents an investigation of the effects of storage stability of radiation sterilized beef. These variables include such factors as type and quality of the raw material, enzyme inactivation techniques, and the use of selected additives.

Dr. H. W. Schultz was the Project Officer and official investigator and Professor R. O. Sinnhuber, Dr. T. C. Yen, and Mrs. Mary Landers collaborators for Oregon State University. The U. S. Army Natick Laboratory Project Officers were Dr. G. D. Gernon and Mr. M. Simon and the Alternate Project Officers were Mr. F. J. Krauss and Dr. F. Heiligman, all of the Food Division.

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ABSTRACT

Results of a series of experiments have led to the development of five (prefried and enzyme-inactivated codfish patties, prefried and enzyme-inactivated halibut patties, and halibut steak) radiation sterilized (4.5 Mrad) seafood products. Large consumer panels judged these products acceptable initially, shortly after irradiation, and after 6 months storage at 21°C. The study included investigation of a large number of variables including (1) thirty commercial brands of breaded seafood products, (2) enzyme-inactivation technique, (3) a large variety of breadings and batter, and binders, (4) methods for preparing the various types of patties, (5) effects of several different anti-browning and antioxidantizing agents, and (6) effects of seasoning and flavor intensifying agents. Both subjective and objective analytical techniques were used for determining the effects of the various factors on acceptability and stability of the products.

SUMMARY

1. This project has led to the development of five radiation-sterilized seafood products; i.e., prefried cod and halibut patties, enzyme-inactivated cod and halibut patties, and halibut steaks. Large panels judged these products acceptable after storage at 70°F for six months.

2. Thirty commercial brands of breaded seafood products that were radiation-sterilized deteriorated during storage at 70 and 100°F due to initial poor quality, autolysis and non-enzymatic browning.

3. Enzyme inactivation of cod muscle, as measured by the formation of amino nitrogen, required a minimum time-temperature heat treatment of 300 seconds at 150°F or 15 seconds at 160°F.

4. A suitable batter (DCA batter mix #4005 for fish sticks) and breader (Modern Maid Redi-breader, medium brown) for irradiated seafood products were selected on the basis of flavor, color and texture.

5. Various methods of comminuting and rates of cooking cod prior to irradiation did not materially affect flavor scores of the stored irradiated product.

6. Cod cakes deep-fried after irradiation scored significantly higher than cakes deep-fried prior to irradiation.

7. Seafood seasoning salt, barbecue seasoning salt, salt, onion salt, garlic salt, MSG and pepper were added to cod fish patties prior to radiation-sterilization. These seasonings improved the flavor of the irradiated patties; textural changes were also noted.

8. Edible binders (29) were screened, and two binders, Viscomix (gelatin by Swift and Co.) and white corn meal, added in combination, were found to improve flavor and texture of irradiated, stored cod patties.

9. Sodium hydrosulfite added to cod cakes did not prevent non-enzymatic browning of the stored, irradiated cakes. Sodium hydrosulfite and calcium chloride, added to ground rockfish, gave no significant color differences between treatments of the stored irradiated fish.

10. Seven antioxidants were evaluated in radiation-sterilized prefried cod cakes by small panels. There were no significant differences in flavor scores of the stored, irradiated cakes.

11. Chemical tests (VOS, TMA and TBA) on stored irradiated cod and rockfish containing antioxidants seemed to indicate that Tenox VI and TDPA would be effective antioxidants.

12. Shortenings and oils (13) recommended for deep-fat frying were irradiated and scored for intensity of irradiated flavor. Spry was selected for further testing. Eight antioxidants added to Spry did not lessen the irradiated odor and flavor.

13. The effect of irradiation on natural fats (Active Oxygen Method) showed that the more saturated fats, such as lard and tallow, were the most susceptible to radiation damage. Vegetable oils showed a 30 to 50% decrease in stability, while fish oils were relatively stable.

14. Irradiation of four antioxidants in Vream (Swift & Co.) revealed that the antioxidants were relatively stable when vacuum packed.

15. The effectiveness of antioxidants varied greatly in prolonging the stability of different fats and oils. This work indicated the usefulness of antioxidants in extending the storage life of land animal fats and possibly of irradiated pork and beef products.

16. High vacuum packing (2 mm or less) of shrimp and shortenings did not yield products of lesser irradiated flavor. However, preliminary work indicated that high vacuum packing improved the flavor of irradiated cod cakes after storage at 70°F for six months.

17. Total volatile bases, pH, TBA number and trimethylamine nitrogen values of irradiated halibut steaks increased with storage time, and showed the value of adding antioxidant, such as TDPA, to the irradiated stored fish.

18. Limited studies of color differences between treatments of stored, irradiated seafood products indicated the advisability of adding an antioxidant, such as Tenox VI, to lessen non-enzymatic browning.

I. General Objectives

The purpose of this contract was to develop radiation-sterilized, shelf-stable fish and seafood products. Sterilization of fish at high levels of radiation frequently imparts undesirable odors and flavors. The general objectives were to investigate various methods of lessening these flavor changes which occur during irradiation and subsequent storage at room temperature. This work was chiefly concerned with the investigation of the following: antioxidants and other additives for the improvement of flavor and storage stability; various methods of preparation and enzyme inactivation; high vacuum packing and other specialized procedures. Subjective methods by taste panel evaluation and objective methods by chemical and physical measurements were employed to evaluate processing variables and treatments.

This final report includes a summary of the work presented in detail in Interim Report #14, File S-590, which was largely the development of radiation-sterilized seafood products. A detailed account of results during the last year are presented herein, dealing primarily with storage studies of the most promising irradiated products.

II. Irradiation of Market Seafood Products

During the initial phase of this contract, thirty commercial brands of breaded seafood products were subjected to irradiation at 4.5 megarad and examined for gross physical and organoleptic changes by small panels. Two of the products, French fried shrimp and prefried fish sticks were evaluated by large panels. Taste panel scores indicated only "borderline" acceptance of the irradiated, stored products. The initial poor quality of some of the products may have been responsible for the rapid deterioration during storage. Autolysis and non-enzymatic browning occurred, batter and breading darkened considerably or became gummy and a tallow-like flavor was noted from the cooking fat. Since no commercial, breaded seafood products seemed to be suitable for radiation-processing, it was decided to embark on product development to overcome these difficulties.

III. Product Development of Breaded Seafoods

Work was initiated on the development of a fish cake or patty which would seem to be the most flexible and adaptable type of product to use for this project. Pacific cod, Gadus macrocephalus, was selected for use in the preparation of ground fish cakes because

it was readily available, economical, bland in flavor and low in fat. The patties were sized to fit round cans (307 diameter) which were used for irradiation and storage. The fish was ground to facilitate the addition of the following: agents to prevent non-enzymatic browning, antioxidants to prevent oxidative rancidity on prolonged storage, and binders and seasonings to improve flavor and texture. Various batters and breadings were tested for irradiation effect on flavor, color and texture. The enzyme-inactivation temperature for fish muscle was determined. Cooking fats and oils containing antioxidants, were screened to determine differences in intensity of irradiated odor and flavor and storage stability. Various methods of preparation, pre-cook and packing of the fish were investigated.

A. Experimental Methods and Procedures

1. Preparation of fish patty, prefried.

Fresh, Pacific cod fillets were ground in a stainless steel meat grinder, using $\frac{1}{8}$ -inch plate. Antioxidants were incorporated in the fish at this point by hand mixing for timed intervals, with the untreated samples receiving the same mixing. The ground fish was stuffed in meat casings (2 $\frac{1}{2}$ x32 E.P. Fibrous Viiking Co.) by means of a hand stuffer. The "sausages" were quick-frozen at -18°F, sliced in 3/8-inch cakes, dipped in batter and breading, and deep fried in hydrogenated shortening at 360°F for three minutes (minimum internal temperature 160°F, 15 sec.). The fried patties were spread on wire racks, quick-frozen and packed in 307x202 "C" enamel cans, three patties per can, sealed and returned to the freezer to await shipment for irradiation. This product was designated a prefried patty, a "heat and serve" item.

2. Preparation of fish patty, enzyme-inactivated.

A second type of patty evolved through our experimental work. This was designated an enzyme-inactivated patty. The variation in procedure is as follows: Binders were added to the ground fish before stuffing in the casings. The "sausages" were cooked in a boiling water bath to enzyme-inactivation temperature, held in a 34°F cooler overnight, sliced in 3/8 inch cakes and packed in cans for irradiation. Parchment paper was placed between the cakes, and the samples were quick-frozen. These patties were breaded and deep fried at time of serving.

3. Irradiation procedure.

After preparation, the frozen samples were shipped under dry ice, via Railway Express, to the Materials Testing Reactor at Arco, Idaho for irradiation at 4.5 megarad, and were returned to Oregon State University under the same conditions. Irradiation was effected in water at ambient temperature. Dose rates varied from 1.67×10^6 to 3.70×10^6 rad/hr average.

4. Storage conditions.

After irradiation the seafood products were stored in controlled temperature rooms at the Department of Food Science and Technology at 70°F for six months. Bacteriological clearance was obtained on all storage samples before presenting them for panel evaluation. The toxicity tests were performed in the Microbiology Department of Oregon State University.

5. Subjective methods of evaluation.

In the organoleptic evaluation of seafood products, two types of taste panels were employed: the small trained panel and the large student panel. The small panel consisted of 6 to 20 staff members and graduate students at the Department of Food Science and Technology, Oregon State University who were trained to recognize irradiated odor and flavor. The students for the large panels were neither trained nor pre-selected, but rather a general notice was posted and 140 to 180 responded at various times. The small panels were used for preliminary evaluations, and the student panels to measure acceptance. These student evaluations may be used as an indication of consumer preferences, since the students show generally the same preference ratings as home consumers, according to Calvin and Sather. (Food Technol., 13, 469, 1959.)

At time of serving the prefried fish patties were heated in a 400°F oven for 12 minutes. The enzyme-inactivated cakes were breaded and deep-fried at 360°F for three minutes. The tasters were served the samples in randomly coded cups with each taster receiving one-fourth of a fish patty per treatment.

Two types of ballots were used for this project. The preference ballot, with a 9-point Hedonic scale, went progressively from a score of 1, indicating "dislike extremely", to a score of 9, indicating "like extremely". A 6-point ballot was also used by the small panel to score intensity of irradiated odor and flavor. The ballot was scored from 0, indicating no irradiated odor or flavor, to 5, indicating very extreme intensity. Statistical analysis of variance was obtained at the 5% significance

level.

6. Objective methods of evaluation.

Objective evaluations by chemical and physical methods were employed. The chemical tests included pH, trimethylamine (TMA)¹, volatile oxidizable substances (VOS)², thiobarbituric acid number (TBA)³ and total volatile bases (TVB)⁴. A Photovolt Photoelectric Reflection Meter, Model 6105, with a tri-green filter, was used to determine color differences between treatments.

B. Treatment Variables

1. Enzyme Inactivation.

The importance of inactivation of the naturally occurring autolytic enzymes of meat to be stored above the freezing point has been clearly demonstrated. However, no report was available on the inactivation temperature of cod muscle enzymes and a study was conducted in our laboratory. Ground cod cakes were heated to internal temperatures of 150, 160, and 170°F for 15, 60, 180 and 300 seconds. It was determined that a minimum time-temperature treatment of 300 seconds at 150°F or 15 seconds at 160°F was required prior to irradiation for inactivation of enzymes in cod by the amino nitrogen method of Pope and Stevens, (Biochem. J., 33, 1070, 1939). Results of this work are in press.

2. Batters and breadings.

Twenty combinations of batters and breadings were tested, not only for irradiation effect on texture, but also for flavor and color. Emphasis was placed on a breading mix that

¹W. J. Dyer, AOAC, Vol. 42, No. 2, 1959

²T. C. Yu (Unpublished)

³Yu and Sinnhuber, Food Technol., Vol. XI, No. 2, pp 104-108, 1957

⁴M. E. Stansby, Ind. Eng. Chem., Anal. Ed. 16, 593, 1944.

⁵Photovolt Corporation, 95 Madison Avenue, New York 16, New York

gave a light brown color during pre-cook to 160°F internal temperature and yielded a desirable medium brown-color after irradiation and reheating. The products were re-cooked by deep frying or heating in the oven before serving. The preferred batter and breader for fish cakes were DCA #4005 batter¹ and Modern Maid Redi-breader, medium brown². This batter and breading were used exclusively in all future research discussed in this report.

3. Methods of comminuting and enzyme inactivation.

In an endeavor to produce a fish patty of more desirable flavor and texture, various methods of comminuting and preheating the fish fillets were investigated as follows:

- a. Chopping in a silent cutter compared with grinding in a meat grinder.
- b. Cooking the fish quickly in a boiling water bath compared with cooking by a gradual increase in water bath temperature to a maximum of 10° above the desired internal temperature.
- c. The use of a Raytheon Radarange, Serial #3, Model 1151, to effect enzyme inactivation at an accelerated rate without otherwise altering the product.
- d. Enzyme-inactivated patty compared with the prefried patty.

Taste panel scores after irradiation indicated that the methods of comminuting and rate of pre-cooking the fish did not materially affect the mean flavor scores. Much developmental work is needed before radar cooking is practicable for the enzyme inactivation of fish. Flavor scores indicated that cakes, deep-fried after irradiation, scored significantly higher than cakes deep-fried prior to irradiation. Deep frying after irradiation seemed to lessen the irradiated odor and flavor and gave a more acceptable product.

¹DCA Food Industries, Inc., 45 West 36th Street, New York 18, New York

²Modern Maid Food Products, Inc., 110-160 Dunkirk Street, Jamaica 12, New York

4. Additives.

a. Seasonings

Seasonings were added to cod fish cakes in an attempt to improve the acceptability of the irradiated cakes. The following combinations of seasonings were tested: 1) salt, pepper, MSG, 2) salt, onion salt, garlic salt, pepper, MSG, 3) Stanga flavoraid smoke salt, 4) Johnny's Seafood Seasoning Salt¹ and 5) Barbecue Seasoning Salt¹. After one month storage at 70°F, a small panel scored the smoke-flavored cake unacceptable. Although the smoke flavor masked the irradiated flavor, it had limited appeal and acquired a medicinal or phenolic taste. With this exception, all of the seasoned cakes received higher scores than the control cake with no seasonings. All of the seasonings tested seemed to have a binding effect, while the control cake tended to fall apart when served. The irradiated cakes containing Seafood Salt and Barbecue Salt seemed to toughen and become slightly rubbery in texture. Salt, pepper and MSG were added to prefried cod cakes in combination with high vacuum packing for large panel evaluation. Results were inconsistent, and it was decided not to add salt to the prefried cakes. Salt, however, was added with the binders, Viscomix and corn meal, to enzyme-inactivated cakes and results are discussed in the following section.

b. Binding agents.

Twenty-nine edible binding agents were screened, including gelatins, starches, gums and algin derivatives. The binders were incorporated in the ground fish at levels from 0.25% to 5.0% and the fish was cooked in the cans in a boiling water bath. The binders were judged on the basis of ease of mixing, free-moisture levels after cooking, flavor and texture scores after irradiation and the ease of handling while slicing and breading prior to frying. The formulation of 4% white corn meal, 1½% Viscomix (gelatin by Swift & Co.) and 0.4% salt of the total weight of the fish was selected for use in enzyme-inactivated fish cakes.

¹Johnny's Dock Restaurant, Tacoma, Washington

c. Browning inhibitors.

The effect of sodium hydrosulfite as a possible browning inhibitor was investigated. Sodium hydrosulfite, at the rate of 100 ppm of sulfur dioxide, was added to the ground fish during preparation of prefried cakes. After 6 months' storage of the irradiated samples, the hydrosulfite samples scored significantly lower in flavor than the control sample with no additive. There was no appreciable color difference between treatments. Sodium hydrosulfite and 0.5% calcium chloride were added separately to ground rockfish. Photovolt readings, using a green filter, were taken after 0, 1, 2, 3, 4, 8, 16 and 24 weeks' storage at 70°F. Three readings were taken on the surface of the rockfish immediately after cutting the cans, and three readings were taken on a center slice and averaged. There were no significant color differences between treatments.

d. Antioxidants.

Antioxidants which are stable toward gamma irradiation and give a definite measure of protection against oxidative rancidity are needed if seafood products are to be stored for prolonged periods. Antioxidants may have a beneficial effect in the prevention of radiation-induced browning reactions.

Four antioxidants at levels of 0.02 to 0.05% were evaluated in prefried cod cakes, in preliminary tests. These antioxidants included Tenox S-1¹ (20% propyl gallate, 10% citric acid and 70% propylene glycol), Tenox IV¹ (20% butylated hydroxyanisole, 20% butylated hydroxytoluene and 60% vegetable oil), 2,4,5-trihydroxybutyrophenone¹ (THBP) and propyl gallate¹ (PG). Results seemed to indicate no appreciable improvement in the flavor of stored, antioxidant-treated, irradiated cod cakes over the control cakes.

Prefried cod patties containing four antioxidants, in combination with citric acid (.001%) and sodium hydrosulfite (0.01% sulfur dioxide), were evaluated by means of trained taste panels and chemical tests after irradiation at 4.5 megarad and storage for six months at 70°F. The antioxidants included Tenox VI¹ (10% BHA, 10% BHT, 6% PG, 6% citric acid, 12%

¹Eastman Chemical Products, Inc., Kingsport, Tenn.

propylene glycol and 56% vegetable oil), THBP, thiadipropionic acid (TDPA)¹ and dihydroquercetin (DHQ)², added at the rate of 50 ppm in the product. Taste panel results gave no clear-cut answers as the value of antioxidant addition to radiation-sterilized seafoods.

Chemical tests included VOS, TMA and TBA determinations, and values are given in Interim Report #14, File No. 8-590. In general, VOS values increased with radiation and decreased with storage time. TMA values increased with radiation and with storage time and temperature. TBA values increased with radiation and decreased slightly with storage. Chemical tests seemed to indicate that antioxidants should be incorporated in radiation-sterilized fish cakes that are to be stored.

Rockfish was selected for further testing of three antioxidants (Tenox VI, TDPA, DHQ) and two browning inhibitors (sodium hydrosulfite and calcium chloride). VOS, TBA and TMA determinations were run after six months storage at 70°F. Results were generally the same as reported in the previous paragraph with prefried cod cakes.

Although the taste panel results and chemical tests were not conclusive, it seemed advisable to add antioxidants, especially when oxygen is present. Other workers have reported this. Such would be the case when samples are packed in large cans for irradiation (i.e. #10 cans). Tenox VI and TDPA were selected as representing two classes of antioxidants for further storage studies.

5. Shortenings and cooking oils.

Radiation sterilization of breaded prefried products frequently gives rise to tallow-like or oxidized flavors which are believed to come from the cooking medium. Thirteen shortenings and cooking oils recommended for deep fat frying were evaluated organoleptically to determine differences in intensity of irradiated odor and flavor. Spry consistently ranked lower in intensity of irradiated flavor than the other brands tested and was used for deep-fat frying. Eight antioxidants were added to

¹Evens Chemetics, Inc., 250 East 43rd St., New York 17, New York
²Forest Products Laboratory, Corvallis, Oregon

Spry¹ at the 0.02% level and the Spry was irradiated at 3.0 megarad to determine whether antioxidants lessen the irradiated odor and flavor in fats. No significant differences were noted between the samples.

The effect of radiation on fats, oils and shortenings was investigated. Fifteen samples of fats and oils were analyzed for decrease in stability by the active oxygen method (AOM), American Oil Chemists Society procedure CD 12-57. Irradiation at 4.5 megarad caused a decrease in the AOM stability of all fat samples. The effect of irradiation on the stability of natural fats appeared to follow a pattern that the more saturated animal fats such as lard and tallow were most susceptible to irradiation damages. The highly unsaturated fish oils showed little change in stability time. The vegetable oils decreased in stability considerably after irradiation, but were not as severely affected as lard and tallow.

Four antioxidants were separately incorporated in xxx Vream², a shortening recommended for deep-fat frying, at levels of approximately 0.02% and 0.05%. The antioxidants included propyl gallate, nordihydroguaiaretic acid, butylated hydroxyanisole and quercetin. The cans were vacuum sealed. There were no appreciable increases in total carbonyls (Berry and McKerrigan), peroxides (Amer. Oil Chem. Soc.), or malonaldehyde (Yu and Sinnhuber) in the Vream samples after irradiation, after three weeks, or after six weeks of storage at 100°F. From 82% to 98% of the irradiated antioxidants were recovered, indicating that irradiation at 4.5 megarad did not severely damage the antioxidants when they were added to xxx Vream. We would anticipate a much greater loss of antioxidants and destruction of the shortening if the irradiation was carried out in the presence of air.

Additional studies were conducted to establish the antioxidant protective factors for both irradiated and non-irradiated fats. The protection factor may be defined as the ratio of AOM stability time of the fat containing antioxidant to the stability value of the control sample containing no antioxidant. The effectiveness of antioxidants vary greatly in prolonging the stability of different oils. Most antioxidants efficiently retard

¹Product of Lever Brothers Co.

²Product of Swift & Co.

the rate of autoxidation of the more saturated animal fats, such as lard and tallow. On the other hand, the addition of antioxidants to vegetable oils and highly unsaturated fish oils gave only a slight increase in stability.

These studies indicate the advisability of adding antioxidants to irradiated seafood products to extend the storage life of the products. Specific antioxidants to be used in fish cakes require further investigation.

6. Vacuum packing.

High vacuum packing (2 mm or less) of shrimp, shortenings and cooking oils did not seem to indicate a lessening of irradiated odor and flavor. However, favorable results with high vacuum packing of fish cakes were obtained. Small panels evaluated prefried cod cakes containing salt, pepper and MSG, packed under high vacuum, irradiated at 4.5 megarad and stored for 6 months at 70°F. On the basis of these scores, it seemed that a prefried cake should be packed under high vacuum. Large panel evaluations were needed to establish the validity of these results.

C. Halibut Steaks

Red Snapper fillets, cod fillets and halibut steaks served with lemon and butter or tomato sauce were screened by small panels. After irradiation at 4.5 megarad, the halibut steaks with tomato sauce received higher flavor scores than the other samples. This product was selected for further irradiation studies.

Whole, fresh-frozen Oregon halibut, Hippoglossus stenolepsis, weighing from 6 to 12 pounds, were sliced in $\frac{1}{2}$ " thick steaks with a band saw while frozen. The steaks were partially thawed, placed in mylar-polyethylene bags and enzyme-inactivated in a hot water bath (170-180°F) to a minimum internal temperature of 160°F. Bone, fat and skin were removed after cooking, and the steaks and liquid from the cook were sealed in 307x202 "C" enamel cans at 25" vacuum. The fish was frozen and shipped under dry ice for irradiation at 4.5 megarad. The halibut was stored at 70°F for six months for organoleptic and chemical evaluations. Chemical tests included TMA, pH and total volatile bases (TVB).

Results indicated that halibut steaks show promise as a radiation-sterilized seafood product. The steaks were lightly covered with tomato sauce and heated in a 400°F oven for 15 minutes to serve the panel. TVB values did not increase with irradiation,

but showed a two-fold increase with storage of the irradiated samples. The pH values increased slightly with irradiation and storage. TMA values increased slightly with irradiation and considerably with storage. It was concluded that halibut steaks be subjected to large panel evaluation.

IV. Storage Studies

A. Subjective Evaluations

The work previous to this point has dealt largely with small panel evaluations of a number of additive and treatment variables. As a logical extension of this research, it was decided to combine the best of these treatments in a series of tests for large panel evaluations. Although most of the work was done with cod, the scope was enlarged to include halibut. After irradiation halibut was found to be superior in texture and lighter in color than cod. However, since halibut has a slightly higher fat content than cod, antioxidants were added to achieve greater storage stability. Activated charcoal packets, as odor scavengers, were included in the cans since other workers have shown them to be particularly effective with irradiated foods. Five products were selected: Prefried cod and halibut patties, enzyme-inactivated cod and halibut patties, and halibut steaks.

1. Materials and Methods

a. Prefried fish patties.

The method as given above was followed in the preparation of the fish patties, with some modifications. After cod or halibut fillets were ground, antioxidants (Tenox VI or TDPA) were added at the rate of 50 ppm. The fish was stuffed in casings, frozen and sliced as previously described. The sliced patties were dipped in DCA #4005 batter and Modern Maid Redi-breader, medium brown and deep fried in Spry, which contained 0.02% BHA. After the fried cakes were packed in cans, a one-gram charcoal packet was attached to the underside of each can lid, protected with parchment paper, and the cans were sealed on a commercial sealer under 29.5" vacuum. After irradiation at 4.5 megarad, the samples were stored at 70°F for 0, 3 and 6 months.

b. Enzyme-inactivated fish patties.

The modifications in the preparation of these cakes were as follows: To each 100 pounds of ground fish were added

4 pounds of corn meal, 1.5 pounds of Viscomix and 0.4 pounds of salt. Tenox VI or TDPA was added at the rate of 50 ppm of the total mix. After the patties were sliced, they were packed in 307x202 cans. Parchment paper was used between the patties and also between the top patty and a one-gram charcoal packet attached to the underside of the lid. The cans were sealed on a commercial sealer at 29.5" vacuum. After irradiation at 4.5 megarad, the samples were stored at 70°F for 0, 3 and 6 months.

c. Halibut Steaks.

The final procedure in the preparation of halibut steaks is as follows: Whole, fresh-frozen Oregon halibut, weighing from 10 to 20 pounds, were sliced in 5/8" thick steaks with a band saw. The steaks were skinned, boned, all visible fat removed and the fish (6½ oz.) was packed in 307x202 cans with parchment paper to prevent sticking to the cans. Five ml. of an aqueous solution of thiadipropionic acid was added so that the concentration was 50 ppm TDPA. The cans were sealed at 29.5" vacuum, cooked in a steam chamber to a minimum internal temperature of 160°F (approximately 18 minutes). The cans were cooked and held frozen until irradiation at 4.5 megarad and storage for 0, 3 and 6 months at 70°F. At the time of serving, the halibut steaks were lightly covered with tomato sauce and heated in a 400°F oven for 15 minutes.

2. Results.

a. Comparison of prefried cod and halibut patties.

Panels were conducted to compare cod and halibut patties after (1) irradiation at 4.5 megarad and (2) storage for six months at 70°F. The storage cakes were served with non-irradiated cakes held at 0°F for six months. Results are given in Table 1.

TABLE 1. Mean Flavor Scores¹ for Prefried Cod and Halibut Patties.

Treatment	Irradiation Level	Storage Temp(°F)	Storage Time (Months)	
			0	6
Cod patties	0 Mrad	0		6.32
Halibut patties	0 Mrad	0		6.64
Cod patties	4.5 Mrad	70	6.42	5.96
Halibut patties	4.5 Mrad	70	6.29	5.82

LSD₀₅ at 0 mon. - 0.25 (159 tasters)
6 mons.- 0.24 (158 tasters)

¹Score 9 high, 1 low

Halibut patties scored significantly higher than cod patties prior to irradiation, but there were no significant differences after irradiation and storage. Although both irradiated samples scored significantly lower than the non-irradiated samples at 6 months, the scores were on the "like" side of the scale.

b. Prefried cod patties.

Panels were conducted to evaluate the effect of irradiation, storage and antioxidants on the acceptance of pre-fried cod patties. Results are given in Table 2.

TABLE 2. Mean Flavor Scores¹ for Prefried Cod Patties Containing Antioxidants.

Treatment	Storage Temp (°F)	Storage Time (months)		
		0	3	6
0 Mrad, w/o antioxidant	0	6.78	5.80	6.15
4.5 Mrad, w/o antioxidant	70	6.00	5.86	6.17
4.5 Mrad, w Tenox VI	70	6.03	6.01	6.19
4.5 Mrad, w TDPA	70	6.10	5.68	6.19
LSD ₀₅ at 0 mon. - 0.23 (151 tasters) 3 mos. - 0.25 (172 tasters) 6 mos. - 0.23 (144 tasters)				

¹Score 9 high, 1 low

The control sample (0 megarad) scored significantly higher at 0 time than the irradiated samples. However, there was no significant preference for the control sample over the treated samples after storage. All scores were within the range of acceptability.

c. Prefried halibut patties.

Large panels evaluated the effect of irradiation, storage and the addition of antioxidants on the acceptance of prefried halibut patties. Results are given in Table 3.

TABLE 3. Mean Flavor Scores¹ for Prefried Halibut Patties Containing Antioxidants.

Treatment	Storage Temp(°F)	Storage Time (months)		
		0	3	6
0 Mrad, w/o antioxidant	0	6.87	6.11	5.88
4.5 Mrad, w/o antioxidant	70	5.66	5.77	5.89
4.5 Mrad, w Tenox VI	70	5.99	5.68	5.94
4.5 Mrad, w TDPA	70	5.88	5.75	5.86

LSD₀₅ at 0 mon. - 0.23 (163 tasters)
 3 mos. - 0.22 (170 tasters)
 6 mos. - 0.23 (156 tasters)

¹Score 9 high, 1 low

The control sample was scored significantly higher than the irradiated samples at 0 and 3 months. After 6 months storage, however, there were no significant differences. The antioxidants did not seem to affect the scores.

d. Enzyme-inactivated cod cakes.

Panels were conducted to evaluate the effect of irradiation, storage and antioxidants on the acceptance of enzyme-inactivated cod cakes. Results are given in Table 4.

TABLE 4. Mean Flavor Scores¹ for Enzyme-Inactivated Cod Cakes Containing Antioxidants.

Treatment	Storage Temp (°F)	Storage Time (months)		
		0	3	6
0 Mrad, w/o antioxidant	0	6.87	6.28	6.42
4.5 Mrad, w/o antioxidant	70	6.83	6.25	6.75
4.5 Mrad, w Tenox VI	70	6.93	6.49	6.60
4.5 Mrad, w TDPA	70	6.78	6.44	6.72
LSD ₀₅ at 6 mon. - 0.23 (146 tasters) 3 mos. - 0.22 (174 tasters) 6 mos. - 0.19 (150 tasters)				

¹Score 9 high, 1 low

Initially there were no significant differences between treatments. After 3 months storage, the samples with antioxidants scored higher than the samples without. All irradiated samples scored higher than the 0 megarc sample after 6 months storage. All were acceptable products.

a. Enzyme-inactivated halibut patties.

Large panels evaluated the effect of irradiation, storage and antioxidants on the acceptance of enzyme-inactivated halibut patties. Results are given in Table 5.

TABLE 5. Mean Flavor Scores¹ for Enzyme-Inactivated Halibut Patties Containing Antioxidants.

Treatment	Storage Temp (°F)	Storage Time (months)		
		0	3	6
0 Mrad, w/o antioxidant	0	7.17	6.33	5.65
4.5 Mrad, w/o antioxidant	70	6.61	6.41	6.53
4.5 Mrad, w Tenox VI	70	6.36	6.37	6.67
4.5 Mrad, w TDPA	70	6.55	6.39	6.71
LSD _{0.05} at 9 mos. - 0.21 (149 tasters) 3 mos. - 0.22 (168 tasters) 5 mos. - 0.23 (157 tasters)				

¹Score 9 high, 1 low

Although the panel preferred the non-irradiated sample initially, this was no longer true after storage. After 6 months, there were no significant differences due to treatments. All samples received scores indicating acceptance.

f. Halibut steaks.

Large panels were conducted to evaluate the effect of irradiation, storage and TDPA on the acceptance of halibut steaks served with tomato sauce. Results are given in Table 6.

TABLE 6. Mean Flavor Scores¹ for Halibut Steaks.

Treatment	Storage Temp(°F)	Storage Time (months)		
		0	3	6
0 Mrad, w/o antioxidant	0	6.68	5.94	6.34
4.5 Mrad, w/o antioxidant	70	5.91	5.30	5.69
4.5 Mrad, w TDPA	70	5.94	5.15	5.53
LSD ₀₅ at 0 mon. - 0.27 (157 tasters) 3 mos. - 0.24 (158 tasters) 6 mos. - 0.21 (159 tasters)				

¹Score 9 high, 1 low

The tasters preferred the non-irradiated halibut steaks to the irradiated steaks at all storage times. However, the irradiated steaks received scores on the "like" side of the scale after 6 months storage. The addition of TDPA did not affect flavor scores.

B. Objective Evaluations.

1. Chemical tests.

The halibut steaks prepared for large panel evaluations were also subjected to a number of chemical tests --- pH, TMA, TBA, and TVB. Determinations were run at each storage time and results are given in Table 7.

TABLE 7. Results of Chemical Determinations on Irradiated Stored Halibut Steaks

Storage & Treatment	Storage Temp(°F)	pH	mg TMAN/ 100 g sample	mg N ₂ / 100 g sample	mg malonaldehyde/ Kg sample
0 months					
0 Mrad	0	6.4	1.4	7.0	10.6
4.5 Mrad					
w/o anti-oxidant	0	6.4	2.5	9.0	10.8
4.5 Mrad					
w TDPA	0	6.4	3.1	9.4	5.9
3 months					
0 Mrad	0	6.3	2.8	9.3	12.9
4.5 Mrad					
w/o anti-oxidant	70	6.4	9.3	14.0	25.0
4.5 Mrad					
w TDPA	70	6.5	9.0	11.9	21.4
6 months					
0 Mrad	0	-	1.2	7.8	22.9
4.5 Mrad					
w/o anti-oxidant	70	-	8.8	17.3	12.7
4.5 Mrad					
w TDPA	70	-	8.5	16.4	11.7

The chemical tests indicated an increase in values due to irradiation and storage. The low TMA and TVB values correlated with the panel scores, which indicated that the halibut steaks were acceptable after 6 months storage. TBA numbers show the value of adding antioxidant to the irradiated, stored fish. TDPA, after

6 months storage, was effective in preventing the formation of a rancid product, malonaldehyde.

2. Color reflectance measurements.

Visual color differences were noted between treatments of the stored, irradiated seafood products. Photovolt readings, using a tri-green filter, were taken on the surfaces of enzyme-inactivated cod and halibut patties after 6-months storage at 70°F. Prefried cakes were sliced horizontally for a reflectance reading of the fish flesh. Four readings were taken on three patties of each treatment. Scores were averaged and results are presented in Table 8. The per cent reflectance for 0 megarad, enzyme-inactivated halibut patties was 62.1.

TABLE 8. Reflectance Measurement¹ of Irradiated Fish Patties Stored for Six Months at 70°F.

Treatment	W/O Antioxidant	With TDPA	With Tenox VI
Enzyme-inactivated cod patties	48.6	46.9	51.8
Enzyme-inactivated halibut patties	44.9	49.3	55.4
Prefried cod patties (Table 2)	40.6	40.1	45.4
Prefried patties (Table 1) cod			43.8
halibut			54.2

¹Per cent reflectance

Table 8 shows the effectiveness of Tenox VI in lessening non-enzymatic browning of the patties.

V. Conclusions

This project has led to the development of five acceptable irradiation-sterilized seafood products that will withstand storage at 70°F for six months. These products are as follows:

- (1,2) Breaded, prefried cod patties and breaded, prefried halibut patties. These products are "heat and serve" items.
- (3,4) Enzyme-inactivated cod patties and enzyme-inactivated

halibut patties. These products are breaded and fried to serve.

- (5) Halibut steaks, served with tomato sauce. This is a "heat and serve" item.